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# *Ab Initio* and DFT Potential Energy Surfaces for Cyanuric Chloride Reactions

by Sharmila V. Pai, Cary F. Chabalowski,  
and Betsy M. Rice

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# Army Research Laboratory

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Weapons and Materials Research Directorate, ARL

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## Abstract

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*Ab initio* and nonlocal density functional theory (DFT) calculations were performed to determine reaction mechanisms for formation of the six-membered ring  $C_3N_3Cl_3$  (cyanuric chloride) from the monomer, cyanogen chloride (ClCN). MP2 geometry optimizations followed by QCISD(T) energy refinements and corrections for zero-point energies for critical points on the potential energy surface were calculated using the 6-31G and 6-311+G basis sets. DFT (B3LYP) geometry optimizations and zero-point corrections for critical points on the potential energy surface were calculated with the 6-31G, 6-311+G, and cc-pVTZ basis sets. Two formation mechanisms of cyanuric chloride were investigated, the concerted triple association (3 ClCN  $\rightarrow$  cyanuric chloride) and the step-wise association (3 ClCN  $\rightarrow$   $Cl_2C_2N_2$  + ClCN  $\rightarrow$  cyanuric chloride). All calculations show that the lower energy path to formation of cyanuric chloride is the concerted triple association. MP2 and DFT intrinsic reaction coordinate (IRC) calculations starting from the transition state (TS) for concerted triple association reaction proceeding toward the isolated monomer resulted in the location of a local minimum, stable by as much as -8.0 kcal/mol, that corresponds to a weakly bound cyclic (ClCN)<sub>3</sub> cluster. The existence of this cluster on the reaction path for the concerted triple association could lower the entropic hindrance to this unusual association reaction mechanism.

## Acknowledgments

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# 1. Introduction

CICN- and HCN-containing munitions were mass-produced in the earlier part of this century. It is expected that aged CICN- and HCN-filled munitions will be uncovered in old disposal sites that are being excavated for environmental cleanup. These cyanide compounds are extremely toxic and must be destroyed. However, there are reports that CICN and HCN can undergo violent reactions and that cylinders containing these agents explode (Aaron et al. 1996). It is crucial that the chemistry behind the initiation of these violent events be characterized before handling these munitions as part of an environmental cleanup.

Although little is known about the details of the reactions, it is well known that CICN and HCN will polymerize after long periods of containment (Migridichian 1947). The primary polymerization product of HCN is the cyclic trimer, *sym*-triazine. CICN polymerizes to cyanuric chloride, the chlorinated analog of *sym*-triazine, as well as to other products, including a tetramer of CICN (Enders 1972). The slow thermal polymerization of HCN to *sym*-triazine is exothermic, and the reaction can be accelerated if the system should reach 184° C (Bretherick 1990). Since the CICN and HCN systems are similar, explosions of containers of CICN have been attributed to acceleration of the polymerization reaction (Aaron et al. 1996), although this has not been proven. Our goals are to determine the low-energy reaction mechanism for the formation of the cyclic trimer from isolated monomer and to quantify the energy release. This information could help determine if the acceleration of the polymerization reactions plays a role in the observed explosions of cylinders containing this agent. Toward this end, we have performed quantum-mechanical calculations to characterize the formation of the cyanuric chloride from isolated monomer.

This is the third of our investigations of polymerization reactions of XCN (where X = Cl or H) to the cyclic trimer,  $X_3C_3N_3$ . The earlier investigations of the formation reactions of *sym*-triazine from HCN provided information about reaction mechanisms and energetics (Pai 1996a, 1996b). Additionally, this system was used to assess the performance of density functional theory (DFT) in comparison with QCISD(T) and MP2 predictions of critical points and reaction path properties

(Pai 1996b). In the current study, we are unable to perform MP2 and QCISD(T) calculations using the largest basis set from the previous study (Pai 1996a, 1996b), cc-pVTZ. However, we are able to perform the same level of DFT calculations for the cyanuric chloride system as in the *sym*-triazine study. Therefore, we have undertaken the detailed comparison between DFT and *ab initio* for the *sym*-triazine system in anticipation of using the large basis set at the DFT level for the cyanuric chloride system. The results of the comparative study using the large basis set established that the B3LYP results are as good (or better) of predictors of energies and properties of critical points along the reaction path for the formation of *sym*-triazine as QCISD(T)//MP2. Therefore, we assume that DFT will treat the chlorinated analog of the *sym*-triazine system with similar accuracy.

The two mechanisms that we assume for the association of XCN to form  $X_3C_3N_3$  are (1) a concerted triple association reaction where three XCN molecules come together in a concerted manner to form the cyclic trimer,



and (2) a step-wise addition mechanism where two XCN molecules first come together to form a dimer, followed by a third monomer that adds to the dimer to form  $X_3C_3N_3$ ,



In this study, we characterize the trimerization reactions of ClCN assuming reactions I and II. Although there are no data available to shed light on the mechanisms of cyanuric chloride reactions, vibrational and structural data of cyanuric chloride are available and allow us to further calibrate our theoretical methods through comparison with experiment. We present both *ab initio* [QCISD(T) and MP2] and nonlocal DFT calculations for critical points on the potential energy surface for formation reactions of cyanuric chloride.

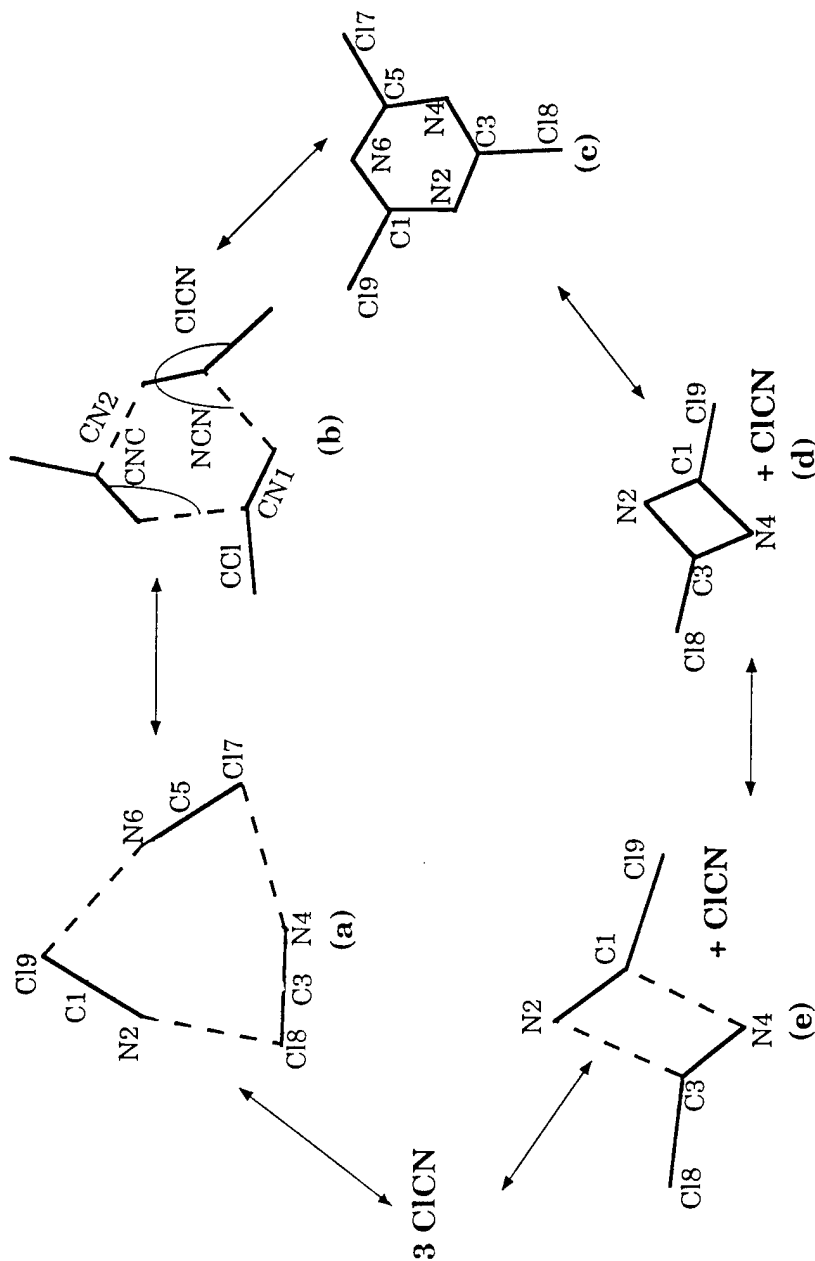
## 2. Methods

All calculations reported herein were performed using the *Gaussian 94* set of programs (Frisch et al. 1995). Structures of critical points were located through geometry optimizations at the MP2 and DFT levels using the 6-31G\* (Hehre, Ditchfield, and Pople 1972; Hariharan and Pople 1973; Gordon 1980) and 6-311+G\* (McLean and Chandler 1980; Krishnan et al. 1980) basis sets. Also, DFT geometry optimizations using the cc-pVTZ basis set (Woon and Dunning 1993; Kendall, Dunning, and Harrison 1992; Dunning 1989) were performed for all critical points on the potential energy surface (PES). All critical points were characterized through normal-mode analyses. Subsequent QCISD(T) energy refinements on the MP2-optimized structures were performed. The DFT calculations used the *Gaussian 94* implementation of Becke's three-term hybrid functional (B3) (Becke 1993) and the Lee, Yang, and Parr (LYP) (Lee, Yang, Parr 1988; Miehlich et al. 1989) correlation functional with nonlocal corrections to both the exchange and correlation functionals. The resulting exchange-correlation functionals are referred to in the text as B3LYP. All geometry optimizations met the default convergence criteria given by *Gaussian 94* (Frisch et al. 1995). All DFT calculations were performed using the default grid size given in *Gaussian 94* (Frisch et al. 1995). Intrinsic reaction coordinate (IRC) calculations leading from the transition states (TS) for reactions I and II were performed to establish reaction paths. The IRC calculations were performed using the 6-31G\* basis set at both the MP2 and DFT levels. The IRC calculations were terminated only when minima were reached as defined by the default convergence criteria of the *Gaussian 94* set of programs (Frisch et al. 1995).

## 3. Results and Discussion

Molecular structures for critical points corresponding to reactions I and II are shown in Figure 1. Table 1 lists the geometric parameters of these critical points. The atom labels in Table 1 are consistent with the labeling on the structures shown in Figure 1. In the following comparisons of calculated structures and frequencies with experiment, we assume that the most accurate *ab initio*

## REACTION I



## REACTION II

Figure 1. Reactions I and II Structures. The (a) Hydrogen-Bonded (ClCN)<sub>3</sub> Cluster Located on the Concerted Triple Association Path; (b) TS for the Concerted Triple Association Reaction (Reaction I); (c) Cyanuric Chloride; (d) Stable Dimer Species Cl<sub>2</sub>C<sub>2</sub>N<sub>2</sub> Associated With the Step-Wise Association Mechanism (Reaction II); and (e) Transition State to the Step-Wise Formation of the Dimer from ClCN (Reaction II). All Structures Except (e) Are Planar. Atom Labels in (a) and (c) Are Consistent With Labels in Table 1.

**Table 1. Geometric Parameters for Critical Points on the Cyanuric Chloride PES**

Parameter	MP2		B3LYP			Exptl <sup>a</sup>
	6-31G*	6-311+G*	6-31G*	6-311+G*	cc-pVTZ	
Cyanuric Chloride						
C1N2	1.3353	1.3338	1.3304	1.3270	1.3247	1.325
C3N2	1.3353	1.3338	1.3304	1.3270	1.3247	1.325
C3N4	1.3353	1.3338	1.3302	1.3269	1.3247	1.325
C5N4	1.3353	1.3338	1.3302	1.3269	1.3246	1.325
C5N6	1.3353	1.3338	1.3303	1.3270	1.3246	1.703
C5Cl7	1.7159	1.7119	1.7331	1.7309	1.7280	1.703
C3Cl8	1.7159	1.7119	1.7329	1.7308	1.7280	1.703
C1Cl9	1.7159	1.7119	1.7328	1.7307	1.7280	112.7
C3N2C1	113.15	113.16	113.14	113.40	113.42	127.4
N4C3N2	126.85	126.84	126.85	126.59	126.57	112.7
C5N4C3	113.15	113.16	113.16	113.42	113.44	127.4
N6C5N4	126.85	126.84	126.85	126.59	126.56	—
N4C5Cl7	116.58	116.58	116.55	116.69	116.72	—
N2C3Cl8	116.58	116.58	116.60	116.72	116.73	—
N6C1Cl9	116.58	116.58	116.57	116.70	116.70	—
TS (I)						
C1N2	1.2078	1.2034	1.1863	1.1806	1.1776	—
C3N2	1.9567	1.9523	2.0331	2.0144	2.0091	—
C3N4	1.2078	1.2034	1.1863	1.1806	1.1777	—
C5N4	1.9567	1.9522	2.0342	2.0155	2.0079	—
C5N6	1.2078	1.2034	1.1864	1.1806	1.1777	—
C5Cl7	1.6697	1.6661	1.6759	1.6737	1.6696	—
C3Cl8	1.6697	1.6661	1.6760	1.6737	1.6694	—
C1Cl9	1.6697	1.6661	1.6758	1.6737	1.6693	—
C3N2C1	119.43	119.98	123.09	123.34	123.34	—
N4C3N2	120.57	120.02	116.93	116.68	116.66	—
C5N4C3	119.43	119.98	123.10	123.32	123.38	—
N6C5N4	120.57	120.02	116.92	116.67	116.67	—
N6C5Cl7	139.75	140.32	144.63	144.22	144.43	—
N4C3Cl8	139.75	140.32	144.58	144.18	144.45	—
N2C1Cl9	139.75	140.32	144.58	144.18	144.51	—
C1CN						
CN	1.1844	1.1787	1.1633	1.1556	1.1533	1.160 ± 0.007 <sup>b</sup>
CCl	1.6380	1.6341	1.6455	1.6408	1.6368	1.629 ± 0.006 <sup>b</sup>
C1CN	180.00	180.00	180.00	180.00	180.00	180.00

<sup>a</sup> Akimoto (1955); Pascal and Ho (1992); Xu, Ho, and Pascal (1994); Maginn et al. (1993).

<sup>b</sup> Values are  $r_e$  (Lafferty, Lide, and Toth 1965).

**Table 1. Geometric Parameters for Critical Points on the Cyanuric Chloride PES (continued)**

Parameter	MP2		B3LYP			Exptl <sup>a</sup>
	6-31G*	6-311+G*	6-31G*	6-311+G*	cc-pVTZ	
Dimer						
C1N2	1.2900	1.2897	1.2857	1.2832	1.2807	—
C3N2	1.5242	1.5220	1.5143	1.5101	1.5081	—
C3N4	1.2900	1.2897	1.2857	1.2832	1.2807	—
C3H8	1.6823	1.6755	1.6959	1.6898	1.6866	—
C1H9	1.6823	1.6755	1.6959	1.6898	1.6866	—
C3N2C1	76.79	77.28	77.40	77.85	77.81	—
N4C3N2	103.22	102.72	102.60	102.15	102.19	—
N4C3Cl8	132.00	132.21	131.62	131.65	131.69	—
N2C1Cl9	132.00	132.21	131.62	131.65	131.69	—
TS (II)						
C1N2	1.2407	1.2378	1.2207	1.2146	1.2114	—
C3N2	1.8892	1.8853	1.9122	1.8993	1.8972	—
C3N4	1.2408	1.2377	1.2206	1.2146	1.2114	—
C3Cl8	1.7064	1.6989	1.7241	1.7182	1.7137	—
C1Cl9	1.7064	1.6992	1.7250	1.7185	1.7139	—
N4C3N2	116.43	115.17	113.00	112.23	111.95	—
N4C3Cl8	138.85	139.51	140.91	141.03	141.66	—
N2C1Cl9	138.85	139.47	140.76	141.00	141.65	—
N4C3N2C4	-150.43	-149.89	-143.02	-144.94	-145.81	—
Cl8C3N4C1	155.76	155.37	153.61	154.00	154.52	—
Cl9C1N2C3	155.77	155.42	153.84	154.03	154.48	—
(ClCN) <sub>3</sub>						
C1N2	1.1841	1.1787	1.1630	1.1555	1.1532	—
C3N2	3.1150	3.1067	3.3944	3.5337	3.6131	—
C3N4	1.1841	1.1786	1.1630	1.1555	1.1532	—
C5N4	3.1169	3.1088	3.3462	3.5068	3.5711	—
C5N6	1.1841	1.1787	1.1630	1.1555	1.1532	—
C5Cl7	1.6342	1.6305	1.6420	1.6370	1.6329	—
C3Cl8	1.6342	1.6305	1.6417	1.6370	1.6328	—
C1Cl9	1.6343	1.6305	1.6419	1.6371	1.6329	—
N6C5Cl7	177.70	178.55	178.67	179.26	179.28	—
N2Cl8C3	67.43	68.16	72.77	76.77	79.45	—
Cl8N2C1	170.14	170.34	164.77	162.25	159.87	—
N2Cl8	3.3525	3.3199	3.4969	3.5287	3.5359	—



and DFT predictions correspond to the largest basis set used at each level (i.e., the MP2/6-311+G\* and DFT/cc-pVTZ results, respectively). MP2 and DFT predictions using smaller basis sets than these are provided in Tables 1–3 to show basis set dependencies, but are not discussed in detail nor compared with experiment.

**3.1 Geometries.** Structural data for gas-phase cyanuric chloride are not available; the only experimental information about the molecular structure of cyanuric chloride comes from electron (Akimoto 1955) and x-ray diffraction studies (Pascal 1992; Xu, Ho, and Pascal 1994; Maginn et al. 1993) of the crystal. The x-ray analysis of the cyanuric chloride crystal by Xu, Ho, and Pascal (1994) indicates that the molecular geometry has approximate  $D_{3h}$  symmetry and that the triazine ring is planar and consists of equilateral C–N bonds (1.325 Å). The triazine ring is not a regular hexagon; the N–C–N and C–N–C angles are reported to be 127.4° and 112.7°, respectively. These structural parameters are very similar to those of gaseous *sym*-triazine (Lancaster and Stoicheff 1956). Pascal and Ho (1992) did not report the C–Cl bond distance. Another x-ray diffraction study by Maginn et al. (1993) provided a mean C–Cl intramolecular bond distance of 1.703 Å and a mean observed NCN angle of 126.23° that differs by 1.2° from that observed by Pascal and Ho (1992). An earlier electron diffraction study of the crystal (Akimoto 1955) provided the following parameter set

$$\text{C–N} = 1.33 \pm 0.02 \text{ Å},$$

$$\text{C–Cl} = 1.68 \pm 0.03 \text{ Å},$$

and

$$\text{N–C–N angle} = 125 \pm 3^\circ.$$

(apparently assuming that the triazine ring is a regular hexagon, which has been shown to be incorrect) (Pascal and Ho 1992; Xu, Ho, and Pascal 1994; Maginn et al. 1993). We report this earlier work because these results were used in the analysis of the crystal vibrational spectrum provided by Thomas et al. (1970), against which we compare our results.

Table 2. Harmonic Vibrational Frequencies (cm<sup>-1</sup>)

Mode	MP2		B3LYP			Exptl
	6-31G*	6-311+G*	6-31G*	6-311+G	cc-pVTZ	
Cyanuric Chloride						
1	142	138	139	139	140	156 <sup>a</sup>
2	168	156	165	163	165	178 <sup>a</sup>
3	168	156	166	164	167	178 <sup>a</sup>
4	213	211	208	208	207	216 <sup>a</sup>
5	213	211	209	208	208	216 <sup>a</sup>
6	411	413	399	398	396	408 <sup>a</sup>
7	474	476	463	464	461	474, <sup>a</sup> 461 <sup>b</sup>
8	474	476	463	464	462	474, <sup>a</sup> 461 <sup>b</sup>
9	509	505	505	505	501	610 <sup>a</sup>
10	646	606	655	651	667	652 <sup>a</sup>
11	646	606	656	651	667	652 <sup>a</sup>
12	796	749	811	815	820	795, <sup>a</sup> 749 <sup>b</sup>
13	877	880	859	859	854	849 <sup>a</sup>
14	877	880	860	860	854	849 <sup>a</sup>
15	995	998	989	993	987	977 <sup>a</sup>
16	1284	1265	1227	1201	1197	1590, <sup>a</sup> 595 <sup>b</sup>
17	1308	1298	1287	1278	1279	1297 <sup>a</sup>
18	1322	1311	1301	1292	1290	1260 <sup>a</sup>
19	1322	1311	1301	1293	1290	1260 <sup>a</sup>
20	1573	1559	1550	1539	1534	1500 <sup>a</sup>
21	1573	1559	1550	1539	1534	1500 <sup>a</sup>
CICN						
1	349	346	392	392	405	378 <sup>c</sup>
2	349	346	392	392	505	378 <sup>c</sup>
3	755	757	741	740	742	744 <sup>c</sup>
4	2154	2135	2326	2310	2311	2216 <sup>c</sup>
TS (I)						
1	584 <i>i</i>	563 <i>i</i>	519 <i>i</i>	529 <i>i</i>	539 <i>i</i>	—
2	71	51	64	69	65	—
3	71	51	65	70	66	—
4	77	65	69	72	69	—
5	144	144	123	121	124	—

<sup>a</sup> Thomas et al. (1970).

<sup>b</sup> Wilson (1973).

<sup>c</sup> Lafferty, Lide, and Toth (1965).

Table 2. Harmonic Vibrational Frequencies ( $\text{cm}^{-1}$ ) (continued)

Mode	MP2		B3LYP			Exptl
	6-31G*	6-311+G*	6-31G*	6-311+G	cc-pVTZ	
TS (I) (continued)						
6	144	144	124	122	124	—
7	264	264	225	227	227	—
8	264	264	225	227	227	—
9	304	303	281	284	283	—
10	456	432	440	441	441	—
11	456	432	441	441	441	—
12	485	459	447	454	460	—
13	487	482	448	454	461	—
14	487	482	479	489	495	—
15	517	521	510	521	522	—
16	732	735	698	694	693	—
17	811	809	762	758	758	—
18	811	809	762	758	758	—
19	1958	1930	2022	1990	1993	—
20	2001	1977	2109	2085	2087	—
21	2001	1977	2110	2086	2087	—
(ClCN) <sub>3</sub>						
1	14	13	8	17	13	—
2	14	14	16	20	18	—
3	24	28	24	24	20	—
4	54	56	33	26	22	—
5	54	56	34	28	25	—
6	63	66	50	38	34	—
7	63	66	51	47	48	—
8	73	78	54	48	49	—
9	98	99	62	53	51	—
10	349	346	395	390	407	—
11	351	346	396	391	408	—
12	351	348	396	394	411	—
13	357	354	399	397	412	—
14	357	354	400	397	412	—
15	361	358	402	399	413	—
16	763	764	748	746	749	—
17	763	764	748	746	749	—
18	763	764	749	747	749	—
19	2159	2138	2328	2310	2310	—
20	2159	2138	2328	2310	2310	—
21	2159	2138	2329	2311	2311	—
Dimer						
1	97	94	102	104	105	—
2	223	223	211	211	211	—

Table 2. Harmonic Vibrational Frequencies (cm<sup>-1</sup>) (continued)

Mode	MP2		B3LYP			Exptl
	6-31G*	6-311+G*	6-31G*	6-311+G	cc-pVTZ	
Dimer (continued)						
3	369	370	361	361	359	—
4	484	472	469	472	469	—
5	487	483	495	500	513	—
6	637	642	614	617	615	—
7	658	654	678	689	691	—
8	904	903	916	908	907	—
9	964	969	947	948	941	—
10	1137	1136	1086	1081	1074	—
11	1645	1621	1582	1562	1559	—
12	1664	1640	1641	1623	1620	—
TS (II)						
1	595 <i>i</i>	598 <i>i</i>	519 <i>i</i>	555 <i>i</i>	570 <i>i</i>	—
2	81	79	88	83	79	—
3	274	272	238	236	236	—
4	326	323	303	303	300	—
5	458	458	435	434	438	—
6	502	494	453	452	446	—
7	538	533	499	496	496	—
8	547	548	508	498	499	—
9	720	715	612	602	599	—
10	842	825	731	708	698	—
11	1724	1698	1800	1781	1782	—
12	1950	1911	1924	1911	1914	—

There is good agreement between the calculated and experimental structural parameters for cyanuric chloride (Table 1). The MP2/6-311+G\* and DFT/cc-pVTZ predictions of all structural parameters are within 1% of experiment. Both methods predict C-N bond distances in the cyanogen chloride molecule that are within 2% or less of the experimental gas-phase values (Lafferty, Lide, and Toth 1965). Both methods predict C-Cl bond distances that are within 0.5% of experiment (Lee, Yang, and Parr 1988; Michlich et al. 1989).

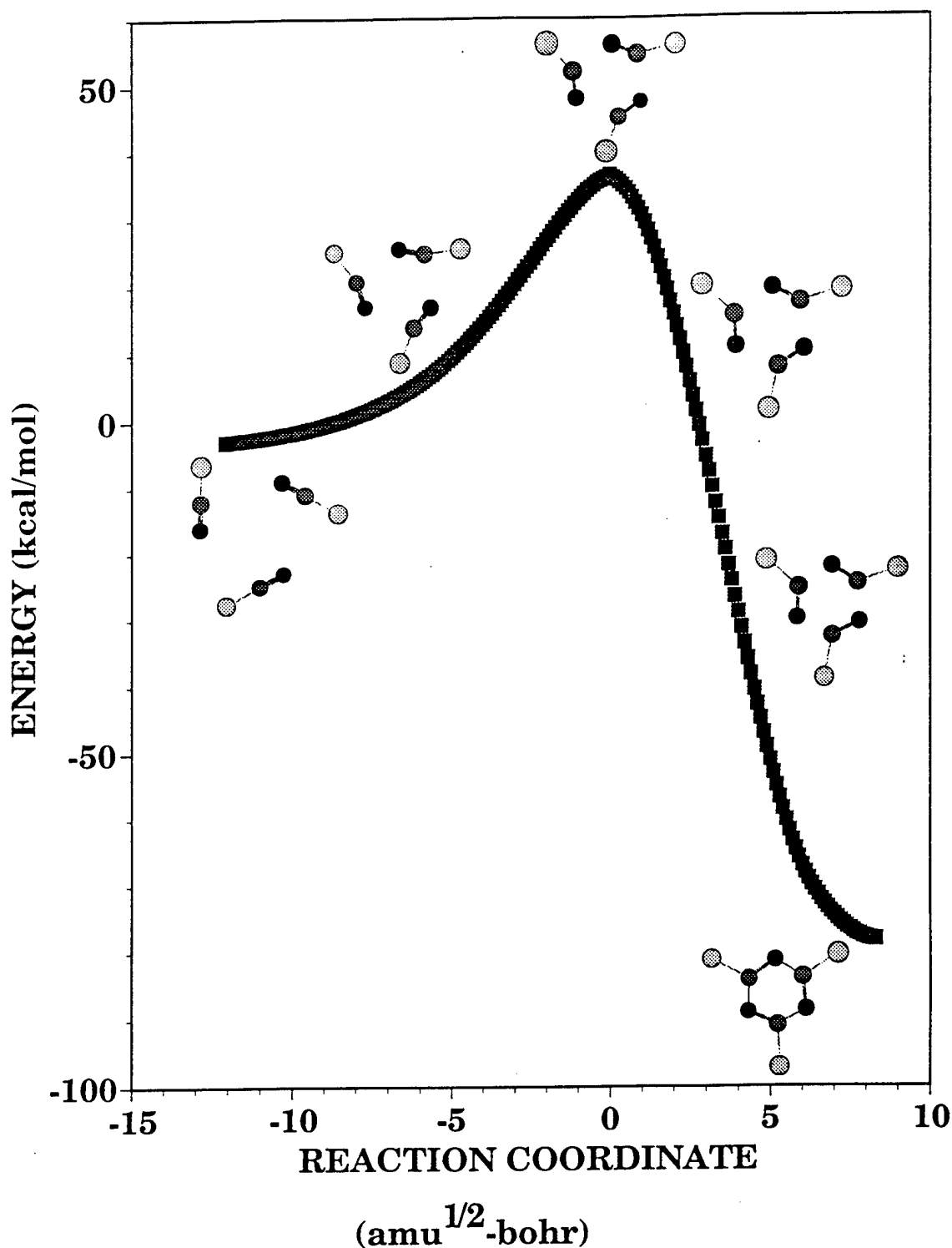
Table 3. Heats of Reaction, Absolute, Zero-Point, and Zero-Point-Corrected Relative Energies on the Cyanuric Chloride PES

Species	MP2		QCISD(T)/MP2		B3LYP		
	6-31G*	6-311+G*	6-31G*	6-311+G*	6-31G*	6-311+G*	cc-pVTZ
Absolute Energies (Hartrees)							
3ClCN	-1656.528659	-1656.742607	-1656.620474	-1656.834437	-1659.024875	-1659.196029	-1659.251138
TS (I)	-1656.465855	-1656.685078	-1656.552678	-1656.772563	-1658.966562	-1659.133727	-1659.184605
Cl <sub>3</sub> C <sub>3</sub> N <sub>3</sub>	-1656.630890	-1656.845927	-1656.72221	-1656.939247	-1659.149350	-1659.307506	-1659.357780
(ClCN) <sub>3</sub>	-1656.539456	-1656.757453	-1656.629530	-1656.848318	-1659.030670	-1659.201592	-1659.256393
Dimer + ClCN	-1656.476237	-1656.692887	-1656.574029	-1656.772103	-1658.988540	-1659.153089	-1659.204679
TS (II)	-1656.423892	-1656.642264	-1656.514318	-1656.713778	-1658.9304540	-1659.096855	-1659.149446
Zero-Point Energies (kcal/mol)							
3ClCN	15.5	15.4	15.5	15.4	16.5	16.4	16.6
TS (I)	17.9	17.6	17.9	17.6	17.7	17.7	17.7
Cl <sub>3</sub> C <sub>3</sub> N <sub>3</sub>	22.9	22.5	22.9	22.5	22.5	22.4	22.4
(ClCN) <sub>3</sub>	16.2	16.1	16.2	16.1	17.1	16.9	17.0
Dimer + ClCN	18.4	18.3	18.4	18.3	18.5	18.4	18.5
TS (II)	16.5	16.4	16.5	16.4	16.4	16.2	16.2
Zero-Point-Corrected Relative Energies (kcal/mol)							
3ClCN	00.0	00.0	00.0	00.0	00.0	00.0	00.0
TS (I)	41.8	38.3	44.9	41.0	37.8	40.4	42.9
Cl <sub>3</sub> C <sub>3</sub> N <sub>3</sub>	-56.8	-57.7	-56.4	-58.7	-72.1	-64.0	-61.1
(ClCN) <sub>3</sub>	-06.1	-08.6	-05.0	-08.0	-03.0	-03.0	-02.9
Dimer + ClCN	35.8	34.1	32.0	42.0	24.8	28.9	31.1
TS (II)	66.7	64.0	67.6	76.7	59.2	62.0	63.4
$\Delta H$ (T = 298 K) (kcal/mol)							
—	-60.0	-60.2	-59.6	-61.2	-74.4	-66.3	-63.4

Structures obtained from MP2 are qualitatively similar to those predicted by DFT for the TS for reaction I, the dimer, and the TS for dimer formation in reaction II. The structures of the TS for reaction I and the dimer are very similar to those of the *sym*-triazine system (Pai, Chabalowski, and Rice 1996a, 1996b). We did not look for the TS for formation of the dimer from the monomers in the *sym*-triazine study since we had eliminated that reaction as the low-energy mechanism after comparing relative energetics of the dimer minima with the TS for three-fold concerted reaction. It was necessary to determine the TS for dimer formation from 2 ClCN, since the energy of the stable dimer (i.e.,  $\text{Cl}_2\text{C}_2\text{N}_2 + \text{ClCN}$ ) lies below or is only slightly higher than TS (I). The structure of this species is nonplanar although the stable dimer is planar. The optimized structure of the  $(\text{ClCN})_3$  cluster is cyclic and has a  $\text{C}_3$  axis of rotation.

**3.2 IRC Calculations.** Energies and structures along the reaction path for concerted triple association determined from B3LYP/6-31G\* IRC calculations are shown in Figure 2. The energies are relative to 3 ClCN. Negative values of the reaction coordinate correspond to the  $(\text{ClCN})_3$  cluster region of the PES, and positive values along the reaction coordinate correspond to the cyanuric chloride region of the PES. The reaction path coordinate value 0.0 corresponds to the TS connecting the  $(\text{ClCN})_3$  cluster and cyanuric chloride minima. The  $\text{C}_3$  axis of rotation of the structures, while not imposed in the calculations, is maintained all along the reaction path.

The greatest difference in structural parameters between the cyanogen chloride and *sym*-triazine systems is in the  $(\text{XCN})_3$  cluster,  $\text{X} = \text{Cl}, \text{H}$ . However, the structures at the TS for the concerted triple association of ClCN to form cyanuric chloride are very similar to those for *sym*-triazine formation: the CN1 and C-Cl bonds have almost the same values as the isolated monomer. Also, the ClCN angle ( $144^\circ$ ) is closer to the cyanuric chloride value ( $122^\circ$ ) than the monomer/cluster value ( $180^\circ$ ). The large difference in the XCN angle between the TS and the XCN monomers was used to explain the substantial vibrational excitation of the bending vibration in the HCN product upon decomposition of *sym*-triazine (Ondrey and Bersohn 1984). Since the features along the IRC for this system are similar to that of the *sym*-triazine system, it is reasonable to predict that vibrationally hot ClCN product molecules, preferentially excited in the bending mode, would be observed upon photodissociation of cyanuric chloride.



**Figure 2.** B3LYP/6-31G\* Energies Along the Reaction Path for Reaction I. The Stable and Transition State Structures and Three Other Structures Along the Reaction Path Have Been Shown to Enable the Reader to Visualize the Mechanism of Concerted Triple Association and Dissociation. The  $(\text{ClCN})_3$  Cluster Is Illustrated in the Far-Left Portion of the Figure. The Cyanuric Chloride Molecule Is Represented by the Far-Right Structure of the Figure.

**3.3 Frequencies.** Table 2 lists the harmonic vibrational frequencies of the critical points for reactions I and II calculated using the *ab initio* and DFT methods and the basis sets mentioned in the previous sections. We present the frequencies of the smaller 6-31G\* basis due to the use of only this basis in all of the IRC calculations.

The most complete vibrational analysis for this system was performed by Thomas et al. (1970). They reported the single-crystal infrared (IR) and Raman spectra for cyanuric chloride at 298 and 77 K and made complete assignments for all fundamentals. Additionally, they performed a normal-coordinate analysis using a modified-valence force-field model and assumed that the triazine ring of the cyanuric chloride is a regular hexagon with all angles equal to  $120^\circ$ . They also assumed the C-N and C-Cl bond lengths given by Akimoto (1955). A fit of this model to the observed frequencies resulted in a set of frequencies and corresponding eigenvectors for the normal modes of cyanuric chloride (Figure 9 of Thomas et al. 1970). Wilson (1973) later analyzed the gas-phase spectrum of cyanuric chloride and changed only a few of the vibrational assignments of Thomas et al. (1970). He reports that, with the exception of  $\nu_{11}$  ( $749\text{ cm}^{-1}$  in gas phase,  $795\text{ cm}^{-1}$  in the solid), the gas-phase spectrum of cyanuric chloride is very similar to the condensed-phase spectra. We were able to match all calculated vibrational modes of the cyanuric chloride to experimental assignments through visual inspection of the eigenvectors when compared to those illustrated in Figure 9 of Thomas et al. (1970). Calculated vibrational frequencies of cyanuric chloride are within  $100\text{ cm}^{-1}$  of the experimental frequencies, with the exception of modes denoted  $\nu_4$  and  $\nu_5$  in Thomas et al. (1970) (modes 16 and 9 here). In the gas phase, these  $A_2'$  modes are inactive and not observed; however, in the solid phase, data for these modes were available and resulted in the assignment of bands at  $1,590$  and  $610\text{ cm}^{-1}$  to  $\nu_4$  and  $\nu_5$ , respectively. For the methods used in this study, the calculated frequencies corresponding to  $\nu_4$  and  $\nu_5$  differ from experiment by  $\sim 400\text{ cm}^{-1}$  and  $\sim 110\text{ cm}^{-1}$ , respectively. A similar large discrepancy between theory and experiment for these two  $A_2'$  modes for *sym*-triazine was found as well (Pai, Chabalowski, and Rice 1996a, 1996b). The predicted frequencies of ClCN agree to within  $100\text{ cm}^{-1}$  of experiment (Lafferty, Lide, and Toth 1965) for all methods and basis sets. There are no measured vibrational spectra for the other critical points.



**3.4 Vibrational Coupling.** In our previous study, we used a method of projecting the vibrational eigenvectors of *sym*-triazine and the symmetric (HCN)<sub>3</sub> cluster onto the reaction path for the concerted triple association reaction Pai, Chabalowski, and Rice (1996a). Our premise in doing so was based on studies that indicate a correlation between the magnitude of the projection of a vibration onto the reaction coordinate and the coupling of that mode with the reaction path (Waite and Miller 1981; Rice, Grosh, and Thompson 1995). For modes that project strongly onto the reaction coordinate, we concluded that these vibrations are possible efficient energy transfer routes between the molecules and the reaction coordinate.

In this study, we provide a similar analysis of the vibrational modes. As detailed in our previous work (Pai, Chabalowski, and Rice 1996a), we calculated local normal modes (Miller, Handy, and Adams 1980) for points along the reaction path for reaction I at the B3LYP/6-31G\* level and projected out the infinitesimal translations and rotations, leaving 3N-7 bound vibrational modes of the molecule plus the eigenvector corresponding to the direction along the reaction path (Miller, Handy, and Adams 1980). We then projected the eigenvectors corresponding to the harmonic vibrational frequencies of equilibrium cyanuric chloride and the (ClCN)<sub>3</sub> cluster onto the eigenvector associated with the direction along the reaction path for selected reaction coordinate values. The results of these projections onto the reaction path eigenvectors are shown in Figures 3 and 4, respectively. Only those modes that have projections greater than 0.05 are shown in these figures. There are five vibrational modes of cyanuric chloride that project strongly onto the reaction path for reaction I; their atomic motions are illustrated in Figure 3. All of these motions exhibit a three-fold symmetric axis of rotation perpendicular to the plane of the triazine ring, and three of them (399, 989, and 1,227 cm<sup>-1</sup>) are similar to the *sym*-triazine vibrational modes that project strongly onto reaction I. Cyanuric chloride has no analog to the remaining *sym*-triazine mode that projects weakly onto the reaction coordinate for reaction I.

There are three vibrational modes for the (ClCN)<sub>3</sub> cluster that project strongly onto the reaction path and three additional vibrational modes that project less strongly. The atomic motions corresponding to these normal modes of vibration are illustrated in Figure 4. A comparison of these

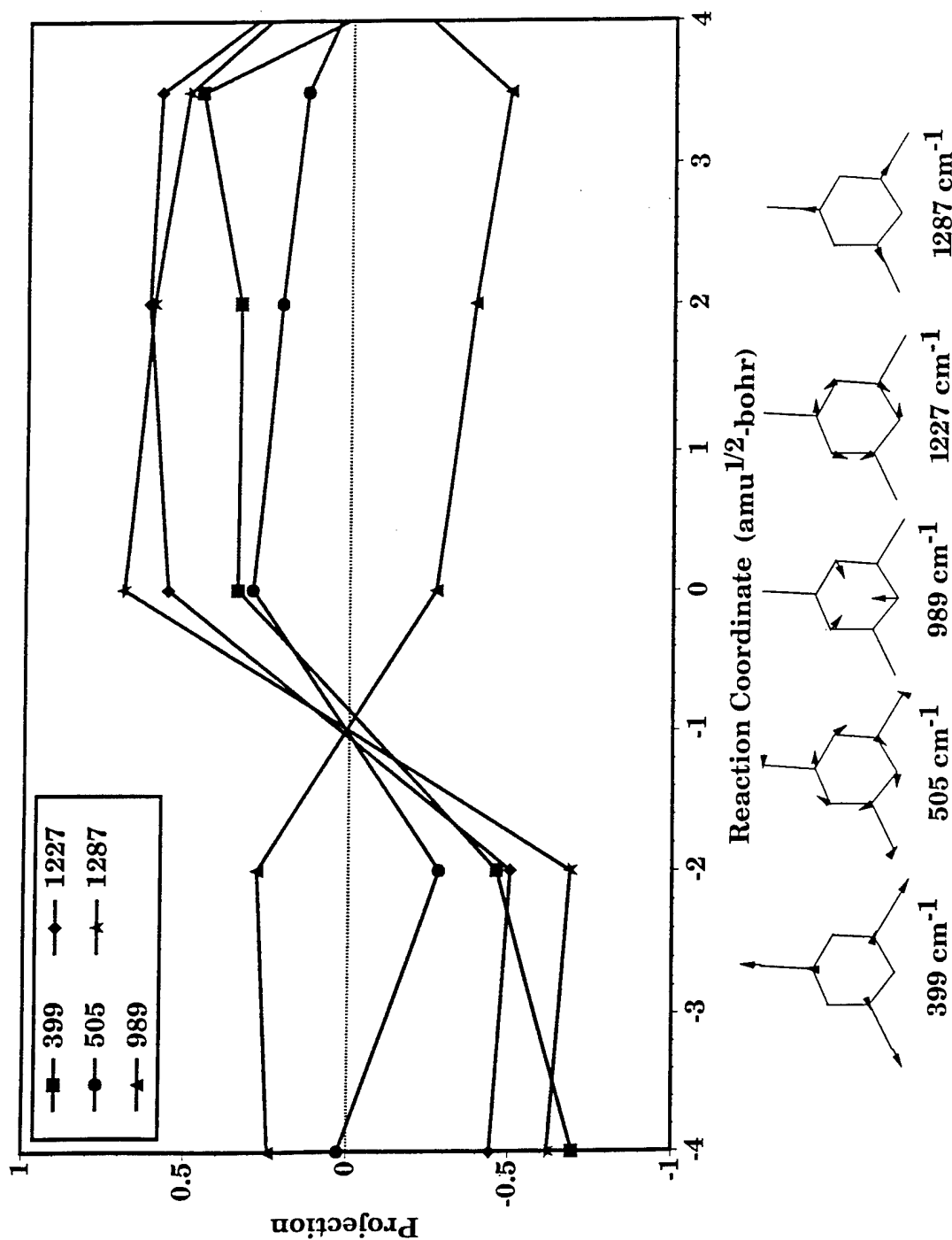


Figure 3. Projection of B3LYP/6-31G\* Eigenvectors Corresponding to Harmonic Vibrational Frequencies of Cyanuric Chloride Onto Eigenvectors That Correspond to the Direction Along the Reaction Path for the Concerted Triple Association Reaction (Reaction 1). Eigenvectors With Projections Greater Than 0.05 Are Illustrated and Labeled With the Corresponding B3LYP/6-31G\* Harmonic Vibrational Frequency (in cm<sup>-1</sup>). The Vibrational Modes Are Illustrated at the Bottom of the Figure.

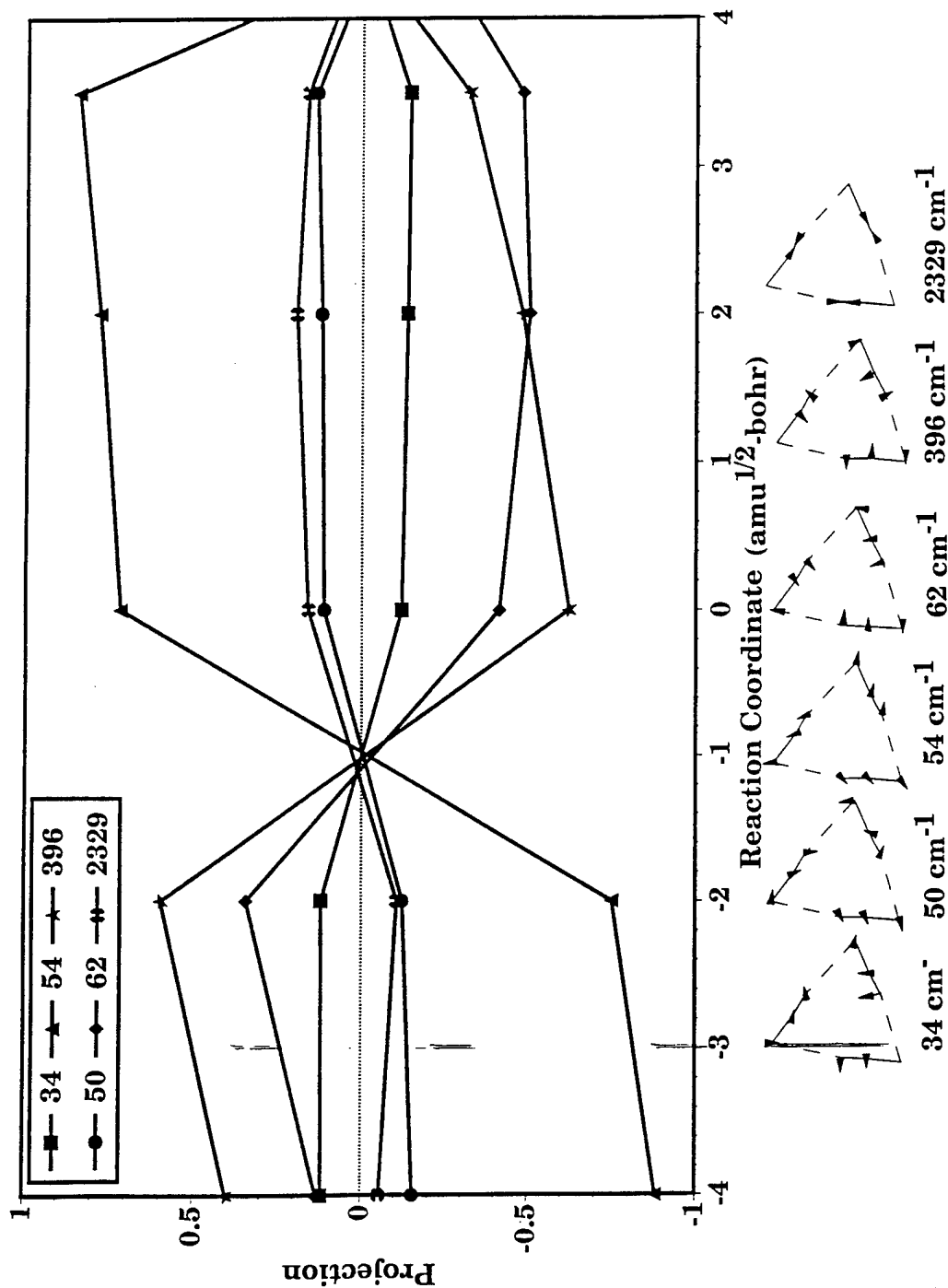


Figure 4. Projection of B3LYP/6-31G\* Eigenvectors Corresponding to Harmonic Vibrational Frequencies of the (CICN)<sub>3</sub> Cluster Onto Eigenvectors That Correspond to the Direction Along the Reaction Path for the Concerted Triple Association Reaction (Reaction II). Eigenvectors With Projections Greater Than 0.05 Are Illustrated and Labeled With the Corresponding B3LYP/6-31G\* Harmonic Vibrational Frequency (in cm<sup>-1</sup>). The Vibrational Modes Are Illustrated at the Bottom of the Figure.

modes with those of the  $(\text{HCN})_3$  cluster that project onto the *sym*-triazine reaction coordinate (Pai, Chabalowski, and Rice 1996a, 1996b) cannot be performed due to the significant differences in the structure of the clusters of the two systems.

As in our previous study, we conclude that the vibrations that project onto the reaction coordinate indicate the most likely routes through which reaction energy distributed in either of these species can transfer efficiently to the reaction coordinate for reaction I.

**3.5 Energetics.** Absolute energies of critical points on the cyanuric chloride PES are given in Table 3. The heats of reaction and the energies of critical points relative to three isolated ClCN molecules are also given in Table 3. All relative energies discussed in this section have been corrected for zero-point energies.

For both methods and all basis sets other than QCISD(T)//MP2/6-311+G\*, the minimum corresponding to the dimer + ClCN is lower in energy than the barrier to concerted triple association. The QCISD(T)//MP2/6-311+G\* results predict that the dimer + ClCN minimum is only 1 kcal/mol higher in energy than the barrier to concerted triple association. This is different than the *sym*-triazine system, in which all methods predicted that the dimer + HCN minimum was higher in energy than the barrier to concerted triple association (Pai, Chabalowski, and Rice 1996a, 1996b). Since our primary goal is to determine the lowest energy pathway to formation of cyanuric chloride, we located the saddle point leading to formation of the dimer from ClCN to determine if it was lower in energy than the barrier to reaction I. At all levels and using all basis sets, the barrier to formation of the dimer is significantly higher in energy than the barrier to triple concerted association. The DFT/cc-pVTZ barrier to formation of the dimer is 63.4 kcal/mol; the DFT/cc-pVTZ barrier to concerted triple association is 42.9 kcal/mol. The QCISD(T)//MP2/6-311+G\* barrier for concerted triple association is 41.0 kcal/mol. The QCISD(T)//MP2/6-311+G\* barrier to formation of the dimer is 76.7 kcal/mol, respectively.

The free energy of activation for these associations includes the effect of entropy, which could be quite important in these reactions. We calculated the free energies of activation for reactions I

and II at the B3LYP/cc-pVTZ level. For reaction I, we calculated the free energy of activation from the cluster minimum. For reaction II, we calculated the free energy of activation from the ClCN reactants. The free energies of activation for reactions I and II are 53.4 and 72.6 kcal/mol, which are 7.6 and 9.2 kcal/mol higher in energy than the respective zero-point-corrected barriers. We also calculated the free energy of activation for reaction I from the three isolated ClCN reactants. The free energy of activation in reaction I at the B3LYP/cc-pVTZ level from the isolated molecules is 61.8 kcal/mol, which is ~19 kcal/mol higher than the zero-point-corrected barrier. It is worth noting that the reduction in the entropic contribution to the free energy of activation by the formation of the cyclic cluster, which significantly increases the probability of this reaction path.

Since the barrier for the formation of the dimer is so much higher than that of the triple concerted association reaction, this mechanism was eliminated as the lower energy path for formation of cyanuric chloride. Therefore, we did not search for the TS for addition of a ClCN molecule to the dimer to form cyanuric chloride. As in the *sym*-triazine system, the lower energy pathway to formation of cyanuric chloride is the concerted triple association. Thermal activation barriers for reaction I or its reverse (concerted triple dissociation) have not been measured. Therefore, we cannot gauge the accuracy of these barrier heights. For the analogous system, *sym*-triazine, the B3LYP/cc-pVTZ barriers were within 6 and 2 kcal/mol of the QCISD(T)//MP2/cc-pVTZ predictions for the forward and reverse of reaction I, respectively.

Both methods show a significant heat of reaction ( $T = 298\text{ K}$ ) for formation of cyanuric chloride (Table 3). The DFT/cc-pVTZ value is -63.4 kcal/mol and the QCISD(T)//MP2/6-311+G\* prediction is -61.2 kcal/mol. In our previous study (Pai, Chabalowski, and Rice 1996b) on *sym*-triazine, we showed that the B3LYP/cc-pVTZ predictions were within a 1.1-kcal/mol agreement with experimental measurements of the reaction enthalpy, which was significantly better than QCISD(T)//MP2/cc-pVTZ predictions. If this trend is maintained for the cyanuric chloride system, the heat of reaction for formation of cyanuric chloride is approximately -63 kcal/mol.

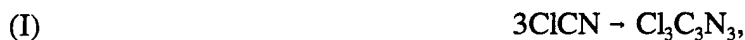
As in the *sym*-triazine system (Pai, Chabalowski, and Rice 1996a, 1996b), reaction path calculations indicate that the weakly bound cyclic  $(\text{ClCN})_3$  cluster is a reaction intermediate to the

formation of cyanuric chloride. Our DFT/cc-pVTZ and QCISD(T)//MP2/6-311+G\* calculations indicate that this species is lower in energy than isolated monomers by 2.9 and 8 kcal/mol, respectively.

These calculations correspond to gas-phase reactions, whereas the XCN (X = H, Cl) in the munitions described in section 1 are compressed to the liquid state. It is well known that reaction barriers can be affected when in solution phase (Hynes 1985, 1994). Therefore, the barriers to association calculated in this study could be an upper limit for reactions of ClCN in aged munitions. Also the cluster is a prereaction intermediate on the concerted triple association pathway and has an arrangement of atoms that is favorable to concerted triple association. This could significantly reduce the entropic hindrance to such an unusual association reaction. Once the barrier is crossed, our calculations indicate that there is substantial energy (~100 kcal/mol assuming gas-phase barriers) available to the translational or internal modes of the product. This amount of energy is sufficient to initiate additional reaction. A translationally "hot" cyanuric chloride molecule in the liquid state could easily transfer energy through collisions with adjacent species (including clusters) in the liquid. The large reaction exothermicity for cyanuric chloride formation and other features of the PES lends support to the suggestion that acceleration of this reaction could contribute to the initiation of explosions of aged containers of ClCN (Aaron et al. 1996).

## 4. Conclusions

We have presented *ab initio* and DFT calculations of formation reactions of cyanuric chloride from isolated ClCN. Two pathways were examined: (1) a concerted triple association reaction,



and a step-wise association reaction, in which a dimer is first formed followed by addition of another ClCN to form cyanuric chloride



Critical points associated with these two reactions were located through MP2 and DFT (B3LYP) geometry optimizations using basis sets of varying sizes and characterized through normal-mode analyses. Energy refinements of the MP2 calculations were done at the QCISD(T) level. Predicted structures were in reasonable agreement with experiment where available. As in previously reported calculations on the hydrogen analog of this system (Pai, Chabalowski, and Rice 1996a, 1996b), the geometry of cyanuric chloride is described extremely well at the DFT level with all three basis sets, which suggests that accurate geometries are available without requiring large basis sets or computationally expensive perturbation techniques. The MP2 and DFT frequencies are within  $\sim 100\text{ cm}^{-1}$  of their corresponding experimental values where available.

The zero-point-corrected DFT/cc-pVTZ energy barrier for reaction II is 63.4 kcal/mol; the DFT/cc-pVTZ energy barrier for reaction I is 42.9 kcal/mol. QCISD(T)//MP2/6-311+G\* barriers are 76.7 kcal/mol for reaction II and 41.0 kcal/mol for reaction I. These results indicate that the lower energy pathway to formation of cyanuric chloride from isolated monomer molecules is through the concerted triple association reaction. Additionally, MP2 and B3LYP IRC calculations for reaction I resulted in the location of a local minimum on the potential energy surface that corresponds to a weakly bound cyclic  $(\text{ClCN})_3$  cluster.

The  $(\text{ClCN})_3$  cluster, whose hydrogen analog was seen experimentally and theoretically determined for the *sym*-triazine system (Pai, Chabalowski, and Rice 1996a, 1996b), is a prereaction intermediate leading to the formation of cyanuric chloride. Its energy relative to isolated ClCN is within the range of  $-2.9$  to  $-8.0$  kcal/mol. The arrangement of the atoms in this cluster removes significant steric hindrance to the concerted triple association reaction. Reaction energy appropriately imparted to the cluster would result in the concerted triple association to form cyanuric chloride.

The heat of reaction for formation of cyanuric chloride ( $T = 298.15\text{ K}$ ) from the B3LYP/cc-pVTZ calculations is  $-63.4$  kcal/mol, in close agreement with the QCISD(T)//MP2/6-311+G\* prediction ( $-61.2$  kcal/mol). This heat of reaction, coupled with the barrier to formation of cyanuric chloride

from  $3\text{ClCN}$ , indicates that, upon traversing the association barrier,  $\sim 100$  kcal/mol energy is available to the product and surroundings.

We also projected the vibrational eigenvectors of cyanuric chloride and the  $(\text{ClCN})_3$  cluster onto the eigenvector associated with the direction of the reaction coordinate at various points along the reaction path for the concerted reaction. For points all along the reaction path, including the TS, five vibrational modes of cyanuric chloride and six vibrational modes of the  $(\text{ClCN})_3$  cluster project onto the reaction path. These projections indicate that certain vibrational modes of cyanuric chloride and the  $(\text{ClCN})_3$  cluster are coupled to the reaction coordinate, suggesting efficient pathways through which reaction energy of either stable species can couple with the reaction path for the concerted association/decomposition reactions. The energy released upon traversing the barrier to formation of cyanuric chloride is sufficient to initiate additional reaction. The large energy release and the prereaction cluster intermediate support the suggestion that acceleration of polymerization reactions of  $\text{ClCN}$  could be contributing factors leading to explosions of aged containers of  $\text{ClCN}$ .



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6. AUTHOR(S) Sharmila V. Pai, Cary F. Chabalowski, and Betsy M. Rice				
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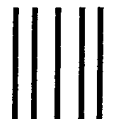
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